UTILIZATION OF WASTE

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WASTE-BEARING DECORATIVE GLAZES FOR FACADE CERAMICS

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Glaze compositions are obtained based on slime from acid sewage regeneration at the Dyat'kovskii Crystal Works, and the technology of producing tinted glass ceramic coatings for facade brick is developed. The main physicotechnical and color characteristics of considered glazes are presented.

Contemporary construction industry has a wide range of strong wear-resistant and durable facade ceramic products for public and residential buildings. However, in a market economy when supply exceeds demand a consumer gives preference to materials that combine diverse structural-texture specifics and coating colors. Such decorative properties can be achieved by varying the heat treatment procedure and the redox condition of synthesis and firing [1], as well as by using the controlled crystallization method involving titanium-bearing components [2]. At the same time, several other urgent problems can be solved: utilization of constantly accumulating industrial waste that is toxic for the ambient medium, expansion of the list of available materials for the glass industry, and assisting the commercial activity of companies.

The purpose of the present study is to develop decorative glass coatings for facade ceramics based on a frit containing a resource-saving component, namely, slime of acid sewage regeneration from the Dyat'kovskii Crystal Works.

For the synthesis of glass coatings we chose the system $SiO_2 – Al_2O_3 – B_2O_3 – Na_2O$, which is one of the main systems for producing white enamels and(or) glazes with different degrees of opacification and luster. Considering a substantial glass-formation area in the specified system [3], the weight contents of SiO_2, Al_2O_3, B_2O_3, and Na_2O were constantly maintained at 50.0, 3.0, 9.5, and 15.5%, respectively, while varying the RO : TiO_2 ratio, which is the deciding factor in the formation of dull and(or) transparent coatings (Table 1).

The initial materials for melting glazes were quartz sand VS-030 (GOST 22551–77), alumina, boric acid, soda, titanium white, and acid sewage regeneration slime from the Dyat'kovskii Crystal Works. Slip was prepared using bentonite clay, technical borax, and color pigments 16/4744, 10/185, 12/350, 11/201, 18/995, and $CuCl_2$ produced by Intercolor (Italy).

Glasses were melted in a laboratory electric furnace in alundum crucibles of capacity 100 cm^3 at a temperature of 1300°C exposing the melt for 30 min at the maximum temperature. Melted glass was granulated in water.

Slip was prepared by moist grinding of components in a ball mill to a residue of 0.1% on a No. 0063 sieve. To produce glass coatings, a slip of moisture 53 – 68%, density 1480 – 1730 kg/m^3, and flow rate of 14 – 18 sec from a viscosimeter of diameter 4 mm was deposited on the facade surface of a ceramic substrate (red facade brick) by casting. Coatings were dried at 120 ± 5°C, firing was performed in a SNOL-1 electric laboratory furnace in a temperature interval of 900 – 1150°C for 15 min.

All coatings had good strength of adhesion to the substrate. At the same time the quality, color, and firing tempera-

TABLE 1

Coating	Mass content, %		Ratio CaO : TiO_2	CLTE, 10^{-6} K^{-1}	Surface tension, N/m	Elasticity modulus, GPa
	CaO	TiO_2				
1	–	22	–	7.0	255	62.7
2	2	20	0.100	7.1	257	63.8
3	4	18	0.220	7.3	259	64.3
4	6	16	0.375	7.5	261	65.7
5	8	14	0.570	7.7	263	66.3
6	10	12	0.830	7.9	267	67.7
7	12	10	1.200	8.1	273	69.1
8	14	8	1.750	8.3	275	70.2
9	16	6	2.670	8.5	276	72.4
10	18	4	4.500	8.7	278	73.9
11	20	2	10.000	8.8	280	74.8
12	22	–	–	8.9	285	75.7

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TABLE 2

Slip composition	Weight content of milling additives (per 100% frit), %			Density, kg/m^3	Type of defect
	clay	borax	water		
1/6	7	5	40	1735	Shivering
2/6	6	6	40	1730	The same
3/6	5	7	40	1725	″
4/6	7	5	45	1720	Thick nonuniform layer
5/6	6	6	45	1715	The same
5/6	5	7	45	1710	″
6/6	7	5	50	1705	Blistering layer, bubbles
7/6	6	6	50	1680	The same
8/6	5	7	50	1650	″
9/6	7	5	55	1610	Blister craters
10/6	6	6	55	1580	The same
11/6	5	7	55	1600	″
12/6	7	5	60	1590	Sags, pinholes
13/6	6	6	60	1550	The same
14/6	5	7	60	1520	″
15/6	7	5	65	1500	No defects
16/6	6	6	65	1490	The same
17/6	5	7	65	1480	″

ture of glaze coatings differed significantly depending on the frit composition (Table 1).

Thus, compositions 10 – 12 yielded clear glazes, regardless of the firing temperature exceeding the second firing temperature (1200°C). At lower temperatures samples had the glaze shivering defect, presumably due to a higher surface tension compared to other compositions. Opalescent coating 9 had discontinuities, whereas glaze coatings 1 – 4 had a rough dull texture. Glasses based on compositions 7 and 8 had beige and light gray tints, respectively. Defect-free white coatings were produced from compositions 5 and 6 with the ratio RO : TiO_2 equal to 0.57 and 0.83, respectively. Their high degree of whiteness (79 and 83%) was achieved due to the formation of sphene crystals (d/n = 4.95, 3.24, 3.00, 2.61, 2.59, 2.29, 2.12, and 2.06 Å) and anorthite crystals (d/n = 4.46, 3.84, 3.31, 3.25, 3.09, 2.99, 2.87, 2.56, 2.50, and 2.42 Å) in the glass matrix. Rutile imparts a yellow shade or a beige tint to coatings 2 – 4 and 7. Composition 6 was found to be the most acceptable for glaze glass coatings. However, the slip components had a perceptible effect on its quality (Table 2).

It can be seen that high-quality coatings with a dull texture and uniform spreading can be obtained in the last there cases, i.e., when the density of glaze suspension is below 1520 kg/m^3. This shows that high-quality coating can be obtained by a more economic method, i.e., by spray deposition. For this purpose we selected composition 15/6 with a lower content of expensive borax as the basis for glazes.

An effective method for the synthesis of dull glazes is controlled crystallization. The crystallization capacity of melt depends on two factors: spontaneous or controlled formation of crystallization centers and their growth rate. Both factors are temperature-dependent. The most favorable conditions for crystallization and, accordingly, for producing white coatings exist in the interval between the temperature maximums corresponding to the seed formation and the crystal growth rate, i.e., within the temperature interval from 800 to 1200°C, which virtually coincides with the second firing temperature: 950 – 1100°C. The lower this temperature limit, the more economic is the glazing technology.

The studies have demonstrated that a defect-free white coating was obtained at a temperature of 950°C with a 15 min exposure. The phase composition of the glaze coating did not vary and was represented by sphene and anorthite, whose crystals are responsible for the dullness effect. However, different pigments had an ambiguous influence on the tone and the firing temperature of coatings, raising this temperature depending on the type of pigment (Table 3). Thus, to achieve more saturated colors, the firing temperature had to be raised by 20 – 40°C. Light-tone shades were obtained

TABLE 3

Pigment	Weight content of milling additives (per 100% frit), %	Color in temperature interval of firing, °C				
		940 – 960	960 – 980	980 – 1000	1000 – 1020	1020 – 1040
16/4744	2	–	Light pink	Pink	Pink	Pink
	3	Light pink	Pink	Bright pink	Bright pink	Bright pink
10/185	3	–	Pale yellow	Light yellow	Light yellow	–
	4	Pale yellow	Yellow	Bright yellow	Bright yellow	Bright yellow
12/350	2	–	Pale blue	Pale blue	Light blue	–
	3	–	Light sky-blue	Blue	Blue	Dark blue
11/201	3	Light yellow	Yellow	Light orange	Light orange	Light orange
	4	Yellow	Light orange	Orange	Orange	Orange
18/995	3	–	Light emerald	Light emerald	Emerald	Emerald
	4	–	The same	Emerald	The same	Dark green
$CuCl_2$	3	–	–	Pale turquoise	Pale turquoise	–
	4	Light turquoise	Turquoise	Turquoise	Turquoise	–

TABLE 4

Parameter	Coating color					
	white	yellow	blue	pink	orange	green
Luster, %	36	35	39	35	36	38
Microhardness, MPa	6550	6380	5980	6220	6180	6240
Fusibility of glaze, °C:						
start of fusing	900	900	900	880	860	880
spreading temperature	960	960	960	940	940	940

* In all cases CLTE is 99.5×10^{-7} K^{-1} and cold resistance more than 30 cycles; whiteness of the white coating 78%.

under low pigment concentrations and decreased firing temperatures (940 – 980°C).

A study of the physicochemical sand service parameters of the obtained coatings indicates that their CLTE agrees with the CLTE of the substrate (99.5×10^{-7} K^{-1}), the glaze luster varies from 35 to 39%, and their microhardness is close to that of glass ceramics made from solid glass: 5980 – 6550 MPa (Table 4).

The synthesized glazes using waste from the Dyat'kovskii Crystal Works are distinguished by their high frost resistance. All parameters of glaze coatings satisfy the requirements of regulatory documents and are preserved as the optimum firing temperature for industrial conditions decreases from 1050 – 1100 to 950 – 1000°C.

REFERENCES

1. A. M. Salakhov, O. V. Spirina, V. I. Remiznikova, and V. G. Khodin, "Low-melting glazes for construction ceramics," *Steklo Keram.*, No. 3, 19 – 20 (2001).
2. R. Ya. Khodakovskaya, *Chemistry of Titanium-Bearing Glasses and Glass Ceramics* [in Russian], Khimiya, Moscow (1978).
3. V. P. Il'ina, "Low-melting glasses based on natural aluminosilicates from Karelia," *Steklo Keram.*, No. 5, 18 – 21 (2002).